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| 14. ABSTRACT During the past decade there has been increasing interest in the Chemistry and Physics of small particles in low temperature electric plasmas. This project aims to study spherical particles with the dimensions of microns (microspheres) levitated in molecular plasmas. A non invasive optical technique, Raman spectroscopy, is being used to probe the surface of the microspheres. Enhancement of the Raman signal will be achieved using whispering gallery modes (wgm's) in the microspheres, where the laser light is entrained at or near the particle surface. A range of particle types will be used in conjunction with different molecular plasmas. The effect of plasma parameters on the molecular structure of the surface of the microspheres will provide fundamental information on plasma-particle interactions. | | | | | |
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Project FA8655-07-1-3033

Laser Spectroscopy of Levitated Microparticles in Molecular Plasmas

Report, 12-31-2007

Abstract:

During the past decade there has been increasing interest in the Chemistry and Physics of small particles in low temperature electric plasmas. This project aims to study spherical particles with the dimensions of microns (microspheres) levitated in molecular plasmas. A non invasive optical technique, Raman spectroscopy, is being used to probe the surface of the microspheres. Enhancement of the Raman signal will be achieved using whispering gallery modes (wgm's) in the microspheres, where the laser light is entrained at or near the particle surface. A range of particle types will be used in conjunction with different molecular plasmas. The effect of plasma parameters on the molecular structure of the surface of the microspheres will provide fundamental information on plasma-particle interactions.

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1. Project Overview

1.1. Objectives

This project aims to develop a non invasive optical technique to study micron sized spherical particles levitated in plasmas. For this we employ the method of Cavity Enhanced Raman Spectroscopy (CERS), which has been very successfully used as a diagnostic method for aerosol droplets [1, 2].

The main objective of this project is to study cavity enhanced scattering from solid microspheres levitated in molecular plasmas where layers are deposited on the particles to gain information about the plasma chemistry and the composition of the deposited layers.

1.2. Status

Different types of microparticles were investigated in order to identify particles suitable for the planned experiments. Silica microspheres can serve as a substrate for coating with Raman-active layers that are smooth enough to support whispering gallery modes and show no Raman scattering themselves in the spectral region of interest. We succeeded in coating silica microspheres with a hydrocarbon layer by means of silanising these spheres with OTS using a wet coating technique. We were able to detect the spontaneous Raman scattering from the deposited layer.

Major changes to the optical setup of the detection system have been implemented. The scattering signal is now detected directly without the use of an optical fibre. This enables us to perform spatially resolved measurements, which greatly improves the assignment of resonances in the spectra. The detection sensitivity has been improved to the point that it is possible to detect the spontaneous Raman scattering from microspheres excited with a 10ns pulsed laser in measurements outside the plasma. For measurements on microspheres levitated in the plasma we improved the signal-to-noise ratio by using a large lens to collect as much scattered light as possible. We were able to measure whispering gallery mode resonances in the fluorescence spectrum of Rhodamine-B-doped MF microspheres enabling us to determine the size of the spheres.

2. Theoretical Background

2.1. Cavity Enhanced Raman Scattering (CERS)

If a droplet (or for that matter a spherical micro particle) is struck by a laser beam, under the right conditions and at particular resonant wavelengths, the light can undergo total internal reflection and become trapped inside the droplet for long periods of time. Long here means on the order of nanoseconds with the result that the light travels a few metres inside the droplet. The trapped laser light leads to stimulated Raman scattering at particular resonant wavelengths within the Raman spectrum. This leads to an enhanced scattering signal at certain wavelengths defined by the particle geometry.

Fig. 1 shows two spectra measured from water droplets. The observed signal depends very much on the illumination geometry. In the left hand figure the laser beam strikes the droplet in its centre, in the right hand figure it is struck tangentially with the result that most of the intensity is coupled into only one resonant mode of the droplet.

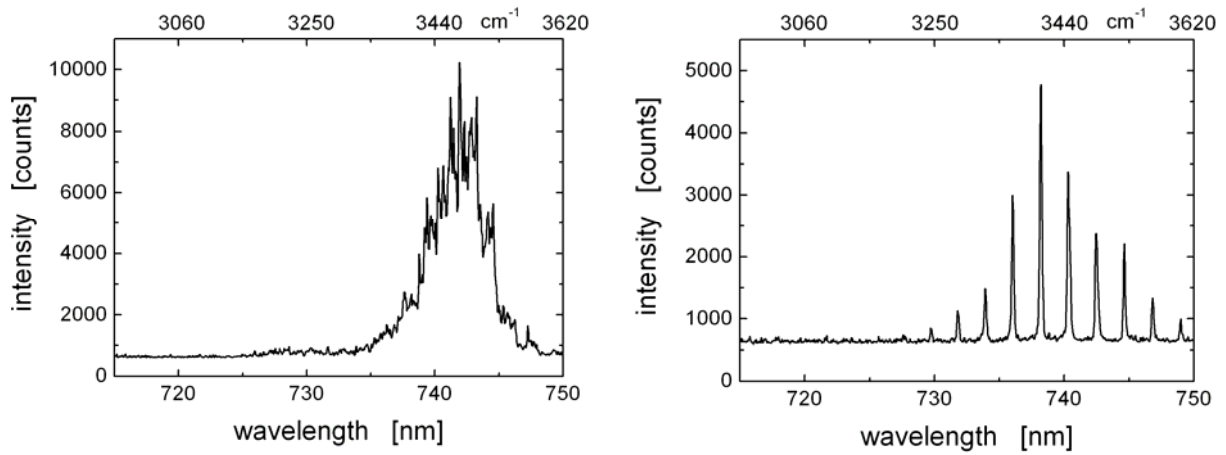


Fig. 1: CERS spectra from water droplets: a) droplet hit at its center b) droplet hit at the edge

Cavity resonances, which are also referred to as **whispering gallery modes** (**wgms**; after the whispering gallery in St. Pauls Cathedral in London), can be thought of as the light forming standing waves inside the particle. They are particular solutions of the MIE scattering problem and can be assigned a mode number, which corresponds to the number of wavelengths in the standing wave, and a mode order, which corresponds to the number of radial intensity maxima. Figure 2 shows two more measurements of water droplets. In the left hand one only resonances of one mode order are excited. The equally spaced peaks belong to resonances of consecutive mode numbers. Resonances of three different mode orders are shown in the right hand diagram; peaks of the same colour belong to the same mode order.

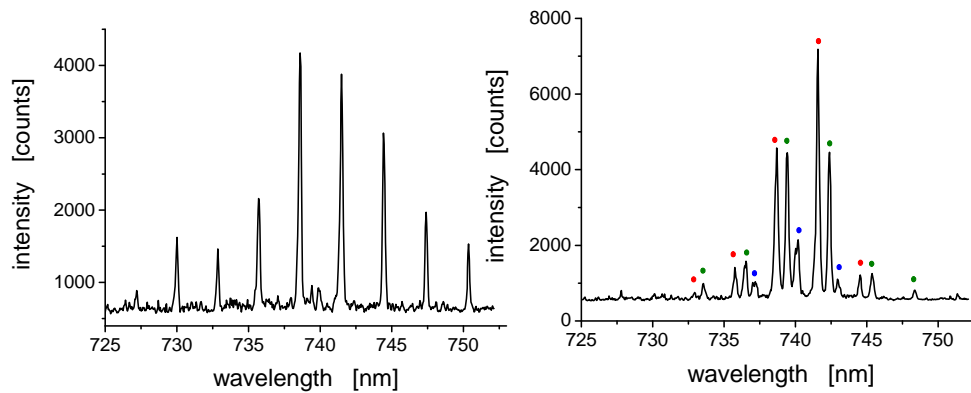


Fig. 2: CERS spectra from water droplets: left hand figure, peaks from one mode order ; right hand figure peaks from three mode orders

2.2. Determination of size and composition

From the spacing between lines belonging to different mode numbers we readily get access to the droplet size.

The following formula gives an approximation for the droplet radius [1]:

$$r \approx \frac{\tan^{-1} \sqrt{m^2 - 1}}{\sqrt{m^2 - 1}} \cdot \frac{1}{2\pi \Delta k} \quad (1)$$

| | |
|------------------|-----------------------------|
| $r \dots$ | radius |
| $m \dots$ | refractive index of medium |
| $\Delta k \dots$ | line spacing in wavenumbers |

With this formula droplet sizes can be calculated with an accuracy of a few hundred nanometres. For higher accuracy still i.e. down to a few nanometres, it is necessary to exactly determine which mode each peak belongs to.

If the droplet composition is not pure water but e.g. a water / ethanol – mixture, in addition to the Raman scattering from water (O-H-stretching band) another peak appears at a wavenumber shift of ca. 2900 cm^{-1} , which corresponds to the C-H stretching band of ethanol (Fig.3). From averaging over many spectra it is possible to determine the concentration of ethanol in the droplet. In fact the Raman signal intensity increases exponentially with the ethanol concentration [3].

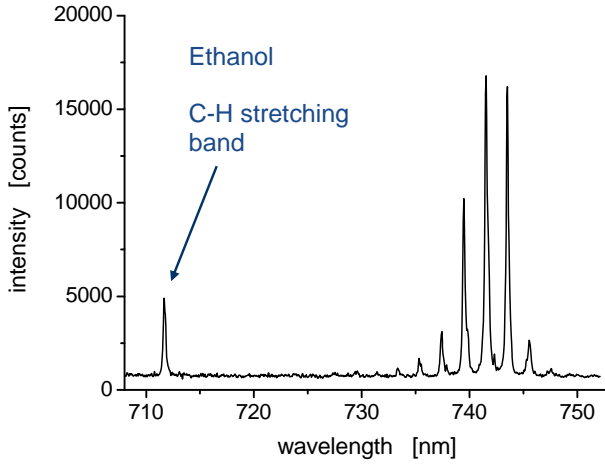


Fig. 3: CERS spectrum from water/ethanol droplets (15 % ethanol). The droplet has a radius of $35 \mu\text{m}$.

2.3. Trapping of micro particles in an RF-plasma

Particles injected into an rf-plasma become negatively charged due to the higher mobility of the electrons compared to the ions. They acquire a floating potential as do all isolated bodies present in a plasma. Depending on their size they can carry several thousand elementary charges.

Several forces act on these charged particles. For bigger particles ($> a \text{ few } \mu\text{m}$) the gravitational force and the electrostatic force are the dominant ones. The particles get confined in the plasma sheath where the electrostatic force caused by the strong fields in the sheath balances the other forces.

A more detailed description of the forces acting on particles in a plasma and on the growing number of applications of dusty plasmas can be found in the literature [4, 5].

3. Experimental Setup

The principal components of the apparatus assembled for the project were as follows.

Laser system:

We used a pulsed tuneable dye laser centred at 590 nm with pulse energies of ca. 1.5 mJ/pulse. To improve the efficiency of coupling into an input resonance of the microspheres the laser linewidth was increased to $0.4\text{nm} \cong 11.5 \text{ cm}^{-1}$ by using a prism and a mirror instead of two gratings in the resonator. The dye laser is pumped by a Nd:YAG-laser (532 nm). It is also possible to use the Nd:YAG-laser directly for the experiments.

Detection system:

A spectrograph "Spectra Pro 2500i" (Acton Research) and an ICCD camera (Andor iStar) were used to resolve and capture wgm-Raman spectra. The signal is sent to the entry optics of the spectrograph via an optical fibre which is positioned at a variable angle with respect to the laser beam. The laser and the ICCD-camera are synchronised using a function generator.

Fig. 4 is a schematic diagram of the experimental arrangement.

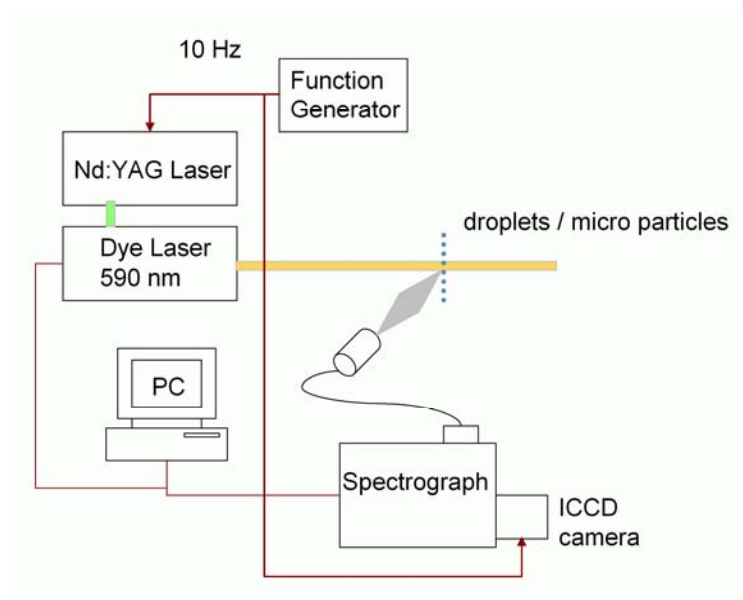


Fig. 4: Experimental schematic

The plasma reactor for trapping and positioning of the microspheres:

For this project we used a custom made plasma reactor, called PULVA-INP [6], which is shown in figure 5. The cylindrical vacuum vessel with a diameter of 40 cm contains two horizontal electrodes (\varnothing 13 cm) separated by 10 cm. The upper electrode is driven at a frequency of 13.56 MHz. The RF power is supplied by a Dressler RF generator in combination with an automatic matching network. Generally, work was conducted at pressures of ca. 10 Pa and RF-powers of 5-10 W. The particles are injected into the discharge and become suspended above the lower electrode. They are illuminated by a spatially broad laser beam at a wavelength of 532nm and viewed orthogonally with a CCD camera. An example is shown in figure 7.

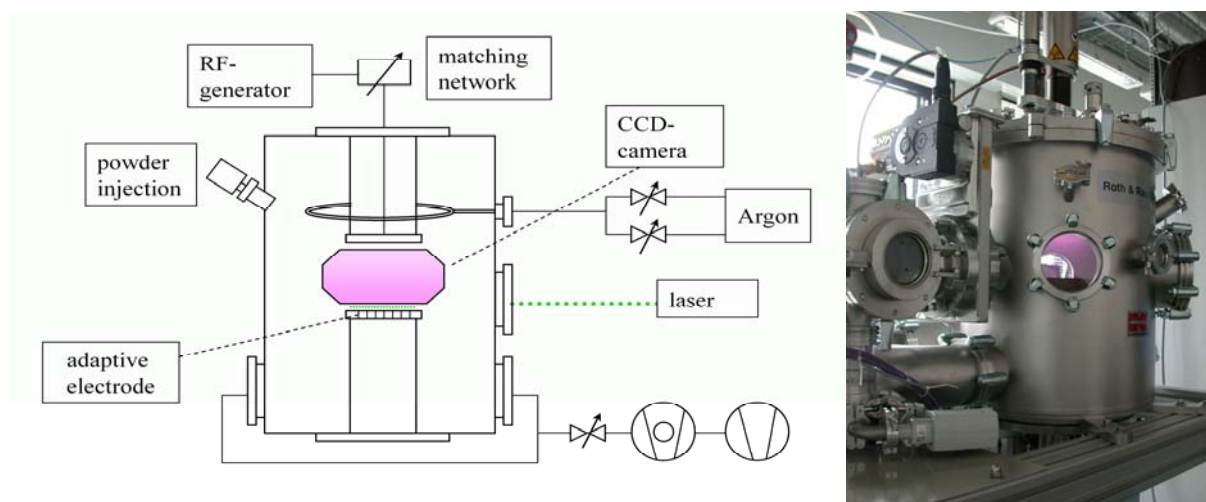


Fig. 5: The experimental plasma reactor PULVA-INP.

The special feature of this reactor is the lower electrode, a so called adaptive electrode (see Fig. 6), which is divided into 101 identical square segments ($7 \times 7 \text{ mm}^2$) surrounded by 4 larger segments and an outer ring electrode. Each segment can be individually biased with a DC-voltage (-100V ... +100V), three of the segments can also generate RF-voltages. This allows precise local manipulations of the plasma sheath and therefore specific manipulation of individual particles (moving and positioning of particles for treatment and diagnostics).

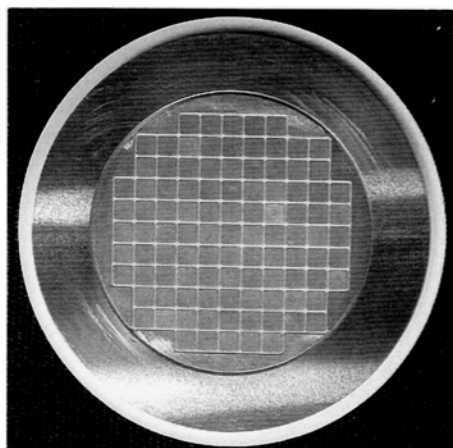


Fig. 6: The adaptive electrode.

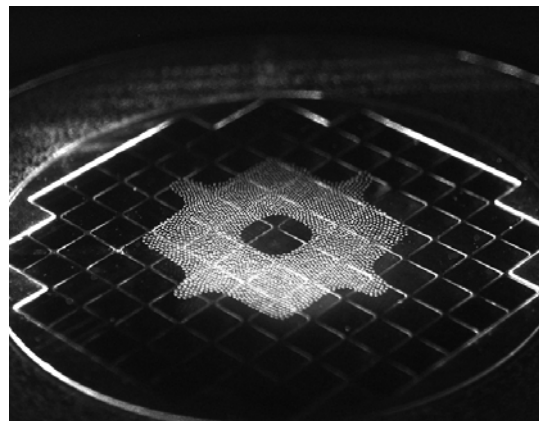


Fig. 7: Micro particles (here: Melamine formaldehyde (MF) – particles with \varnothing 10 μm) levitated in an Argon-rf-plasma above the adaptive electrode. Negative bias voltage is applied to the central segment and to the segments surrounding the particles.

Optical Setup:

A major change was made to improve the optical setup. Earlier we used an optical fibre to detect the scattered signal. We found that the signal intensity especially from particles levitated in the plasma was too low. One reason for this lies with the intensity loss in the optical fibre. We changed the setup for direct imaging of the scattered light via the front entrance of the spectrograph. A schematic drawing of the arrangement for measurements in air is shown in fig. 8a. The laser is focussed on the sample from below and at an angle of 90° with respect to the laser beam and the scattered light is imaged onto the entrance slit using a 50mm-lens. A coloured glass filter is used to block the laser wavelength itself. With this setup we gained the important advantage of being able to achieve spatially resolved measurement. This allowed us to distinguish between the scattering signals arising from different individual microspheres.

Setup for measurements on microspheres levitated in the plasma

For measurements in the plasma it is essential to increase the signal intensity as much as possible. The path length from the levitated microspheres i.e. the signal source, to the spectrograph is much longer than in the experiments in air. The excitation laser is focussed on the microspheres which are levitated in the center of the reactor chamber using a lens with a focal length of 300 mm. To collect as much scattered light as possible a large lens with an effective diameter of 10 cm was installed in front of the window of the plasma reactor. A second lens with a focal length of ~ 40 mm was used to make a parallel beam which is then guided by a set of mirrors to the spectrograph and focussed onto the entrance slit.

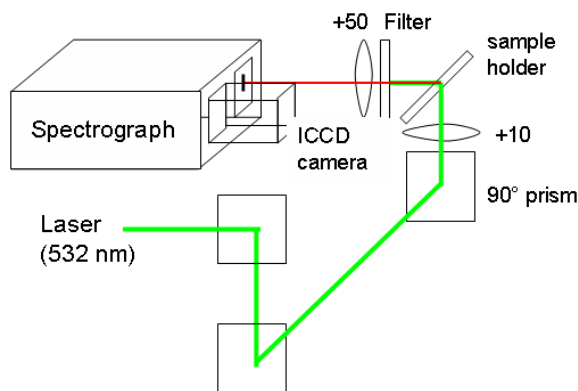


Fig. 8a: Optical setup for CERS-measurements on microspheres in air.

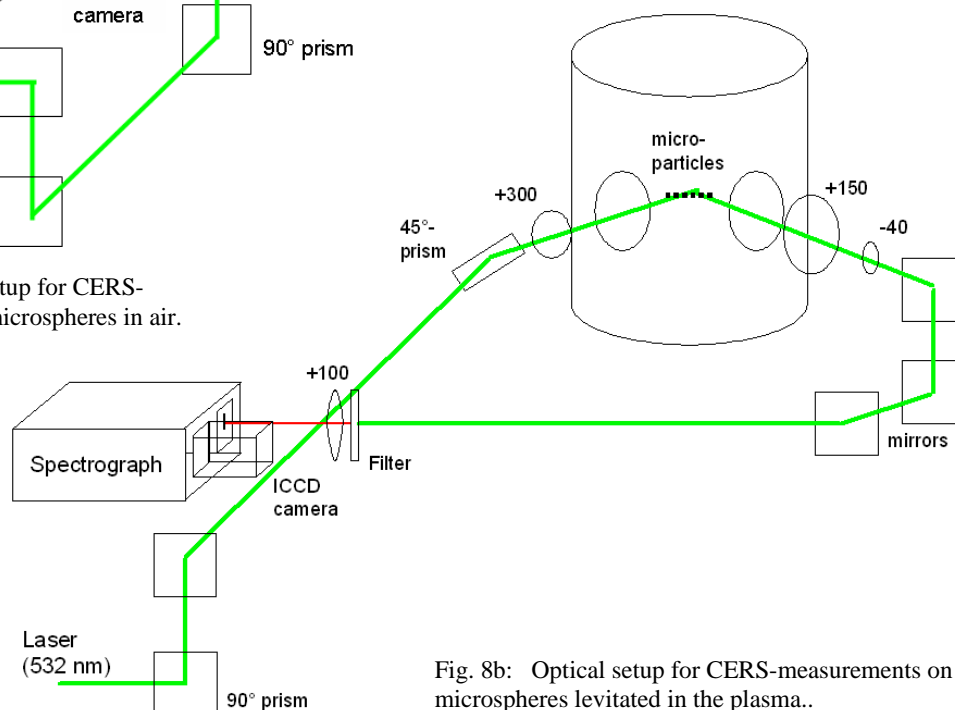


Fig. 8b: Optical setup for CERS-measurements on microspheres levitated in the plasma..

4. Results

4.1. Detection system improvements

Spatially resolved measurements of cavity enhanced fluorescence

With the changes to the optical setup to image the scattering signal directly onto the entrance slit of the monochromator we gained an important advantage. We are now able to spatially resolve the signal. This means it is possible to distinguish between signals coming from different particles, which is essential for identifying the resonances without the complication of resonances in the same spectrum coming from different particles.

Figure 9 shows the fluorescence signal from Rhodamine-B-coated silica spheres as recorded with the ICCD camera connected to the spectrograph. The laser focus is so large that more than one sphere is illuminated when they are close to each other. The optical setup for these measurements is shown in fig. 8. It can be seen in fig. 9 that two different particles are emitting a cavity enhanced fluorescence signal. The distance between resonances of consecutive mode order is higher for particle 2 compared with particle 1. This means that particle 2 is a little smaller than particle 1. The calculated radius is given in fig. 10.

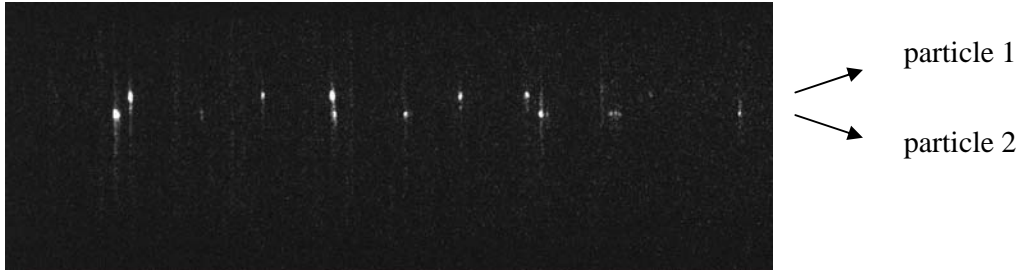


Fig. 9: CCD image of the fluorescence signal from Rhodamine-B-coated silica spheres. The vertical direction corresponds to the spatial resolution, the horizontal direction gives the spectral resolution (ca. 645 - 605 nm from left to right).

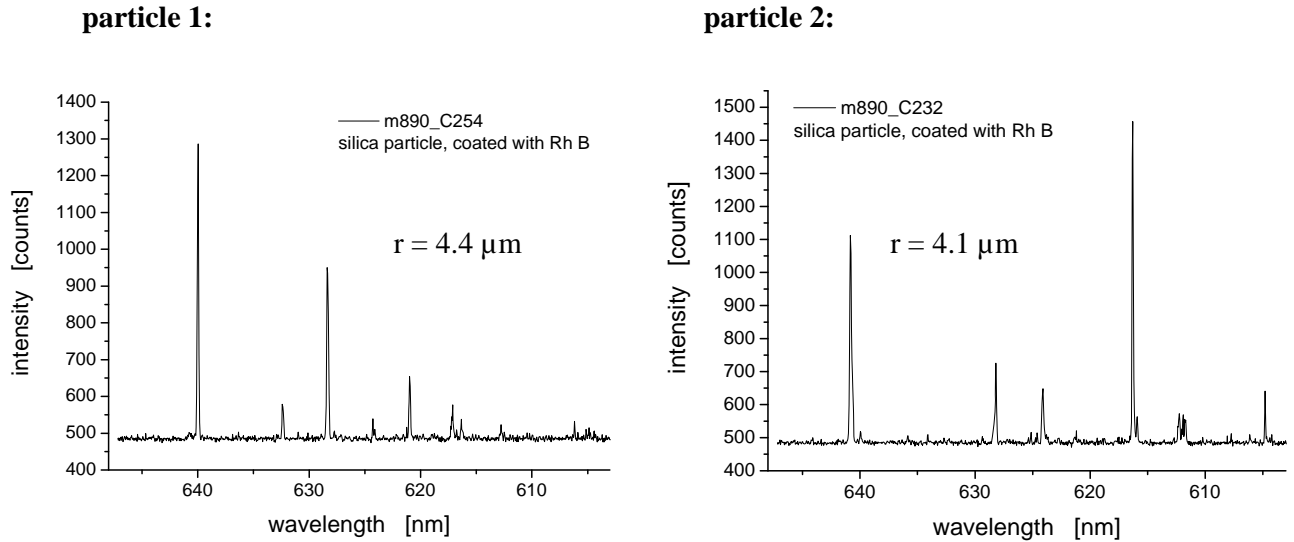


Fig. 10: spectrum from the upper (1) and the lower (2) particles in the picture in Fig. 11.

Improvement in detection sensitivity

After the improvement in the optical setup we were able to measure the spontaneous Raman scattering from microspheres even when using the pulsed excitation laser. Although the laser pulses have a relatively high energy, they have a duration of only 10 ns which is a very short time for the acquisition of the scattering signal. In previous experiments on microspheres in air it has not been possible to detect any spontaneous Raman scattering using the pulsed laser. Now we measure a very weak signal which can be improved by accumulation of many measurements using the photon counting feature of the ICCD camera. Figure 11a shows the Raman spectrum of PMMA spheres with a diameter of 20 μm . We see the typical PMMA Raman spectrum. These microspheres have a very rough coating of melamine formaldehyde (see figure 11b) which, not unexpectedly, makes it impossible for the spheres to support whispering gallery modes. Hence any Raman scattering that is measured is not enhanced by cavity resonances.

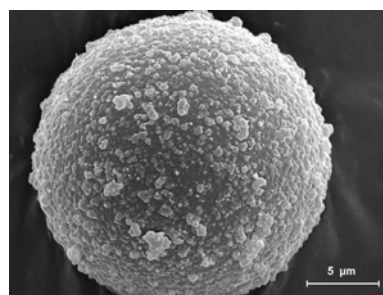
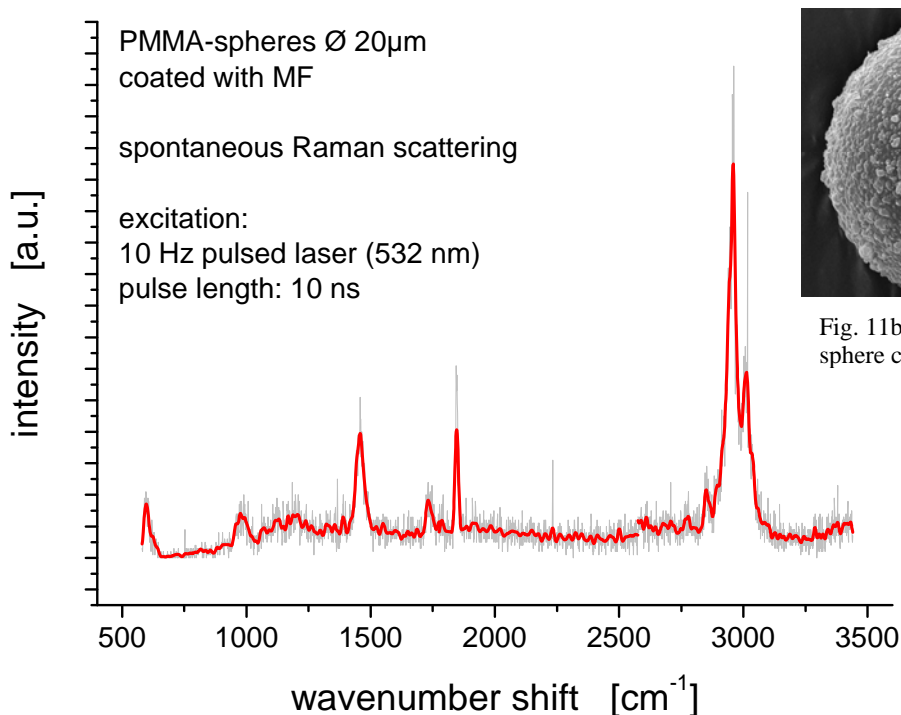


Fig. 11b: SEM picture of a PMMA-sphere coated with MF.

Fig. 11a: Raman spectrum of PMMA spheres coated by a rough layer of melamine formaldehyde. 400 measurements were accumulated (photon counting) with an effective integration time of 10 ns each.

4.2. Investigation of various particles in air

The experiments on aerosol droplets that were carried out in the preceding project were very successful and cavity enhanced Raman spectra could be easily obtained. In contrast it proved much more difficult to get successful measurements from solid particles.

Microspheres suitable for our investigations need to satisfy two basic conditions:

- It has to be possible to trap them in the rf plasma. This means they have to be light enough, so their diameter has to be smaller than ca. 20 μ m, depending on the material.
- They have to be smooth enough to support WGMs.

We investigated solid particles of various sizes and from various materials (see interim report 1, item 0002 for more details) to find suitable particles. Firstly we needed microspheres that showed good Raman scattering with strong and broad enough bands to excite whispering gallery modes. Secondly we needed microspheres that did not show Raman scattering that could be used as a substrate for applying coatings that did show Raman scattering.

To test the particle smoothness we coated them with Rhodamine-B-solution and tested whether we could observe whispering gallery modes in the fluorescence coating. Additionally, pictures of the particles were taken using a scanning electron microscope. To see in which spectral range cavity enhanced Raman scattering could be expected, the spontaneous Raman scattering of the micro particles was measured using a 532nm-cw-laser.

We identified PMMA-spheres as microspheres that showed good Raman scattering. As microspheres with a surface coating we used silica particles with a hydrocarbon coating.

4.2.1 PMMA (Polymethylmethacrylate) particles (microparticles GmbH) Ø 10, 21, 36, 50, 150 µm

The PMMA particles do not levitate well in the plasma. It is difficult to trap particles with a diameter of 20 µm; on the other hand 10-µm-particles can easily be trapped. The particles are very smooth, their size distribution is excellent, they show Raman scattering at about 2900 cm⁻¹. It is straightforward to excite cavity enhanced Raman scattering (whispering gallery modes). Rhodamine B coated particles also show cavity enhanced fluorescence.

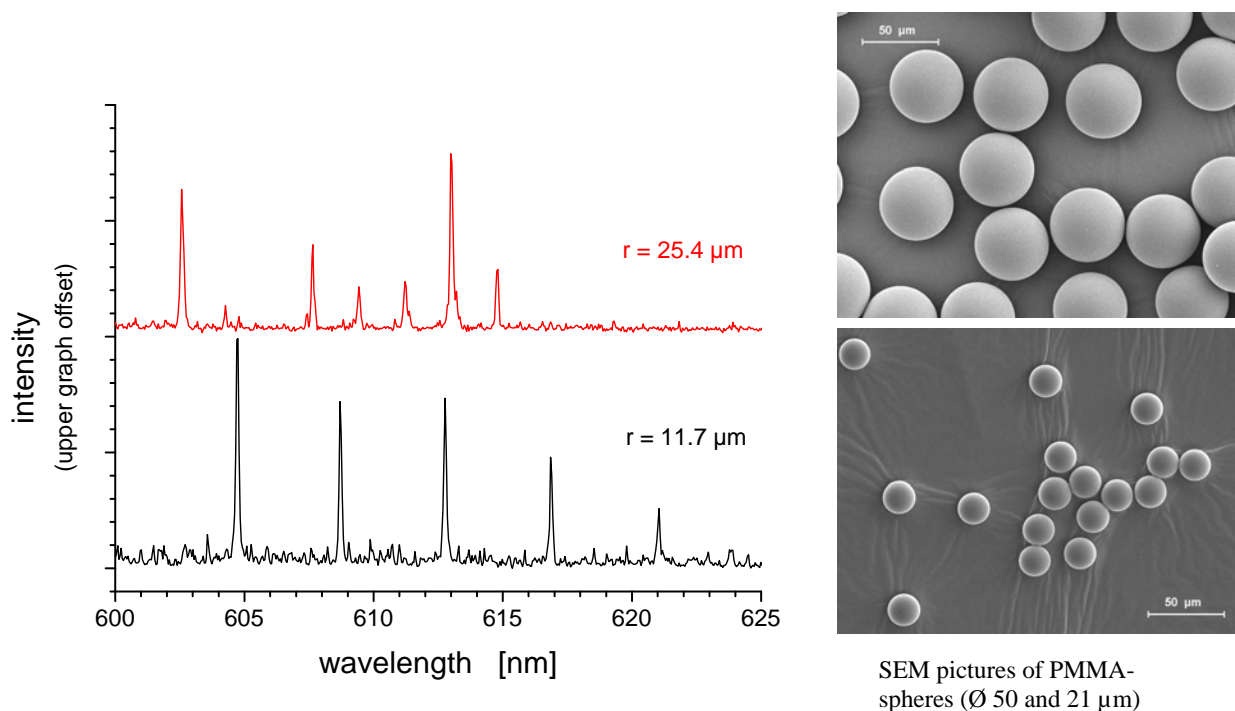


Fig. 12: cavity enhanced fluorescence spectra of RhB-coated PMMA-spheres

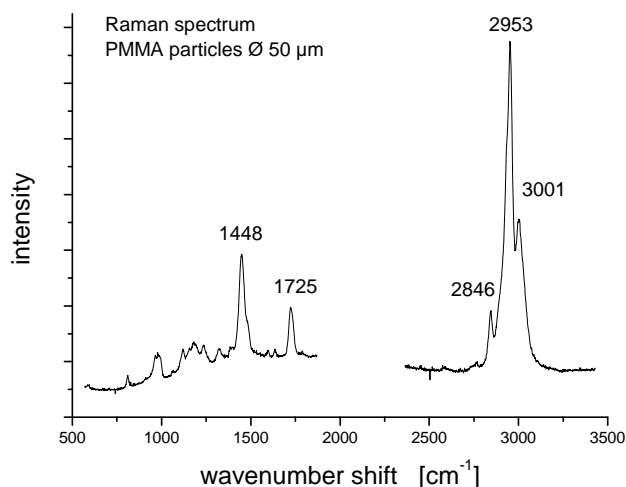


Fig. 13: Raman spectrum of PMMA particles (integration time 0,5s *100)

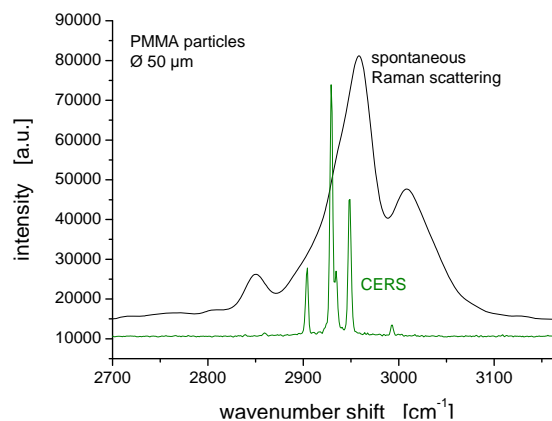


Fig. 14: cavity enhanced Raman scattering on PMMA particles in comparison to the spontaneous Raman scattering.

4.2.2. Hydrocarbon-coated microspheres

To investigate microspheres with hydrocarbon layers deposited onto them we need a substrate that shows little or no Raman scattering itself, so that it is possible to detect the Raman signal from the surface layer only. For this purpose different silica microspheres were used. They show no Raman scattering in the region of the C-H stretching band at a wavenumber shift of ca. 3000 cm^{-1} (see figure 15). Different methods for coating those spheres were employed, firstly: coating in an Argon-Methane plasma, and secondly: silanising the microspheres with octadecyl trichlorosilane (OTS).

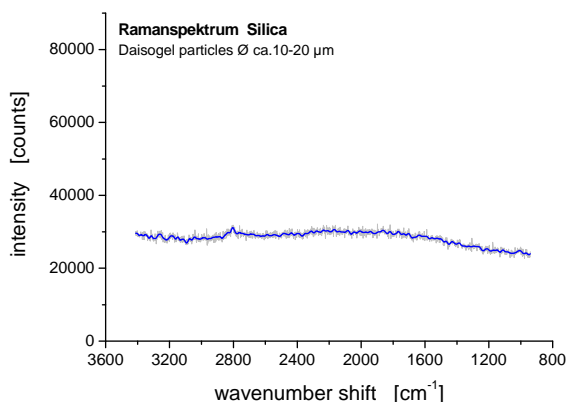


Fig. 15: Raman spectrum of silica particles (integration time 0,5s *100)

Plasma-coating of silica microspheres

The first attempt was to coat the silica spheres in an Argon-Methane plasma. For the coating process the particles were put on a glass substrate and placed inside an rf-plasma reactor. The plasma conditions were chosen in a way that a 50 nm thick layer should be formed. After treatment both the microspheres and the glass substrate showed a complete dark layer in the visible.

Investigation with an electron microscope showed that the coating is very rough (see fig. 16). This coating method seems inappropriate for our purposes, since the detection of a cavity enhanced signal requires a much higher surface smoothness.

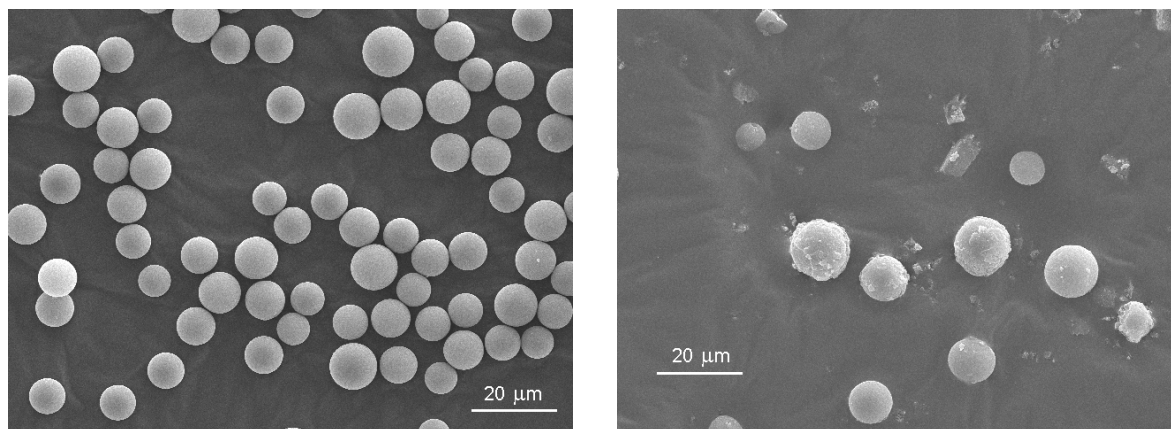


Fig. 16: SEM picture of silica microspheres. Left side: uncoated. Right side: coated with a hydrocarbon layer in an Argon-Methane plasma.

Silanising of silica microparticles

The second method for coating microspheres with a hydrocarbon layer that was employed was silanising with octadecyl trichlorosilane (OTS). This coating should be intrinsically much thinner since only a monolayer of hydrocarbon is bonded to the surface. Figure 17 shows electron microscope pictures of the uncoated and the silanised spheres. There is almost no visible difference between the coated and uncoated spheres. The treated particles are still as smooth as before. If they are additionally coated with Rhodamine B they show clear and strong resonances in their fluorescence spectrum (see fig. 18). This shows that their surface is still smooth enough to support whispering gallery mode resonances.

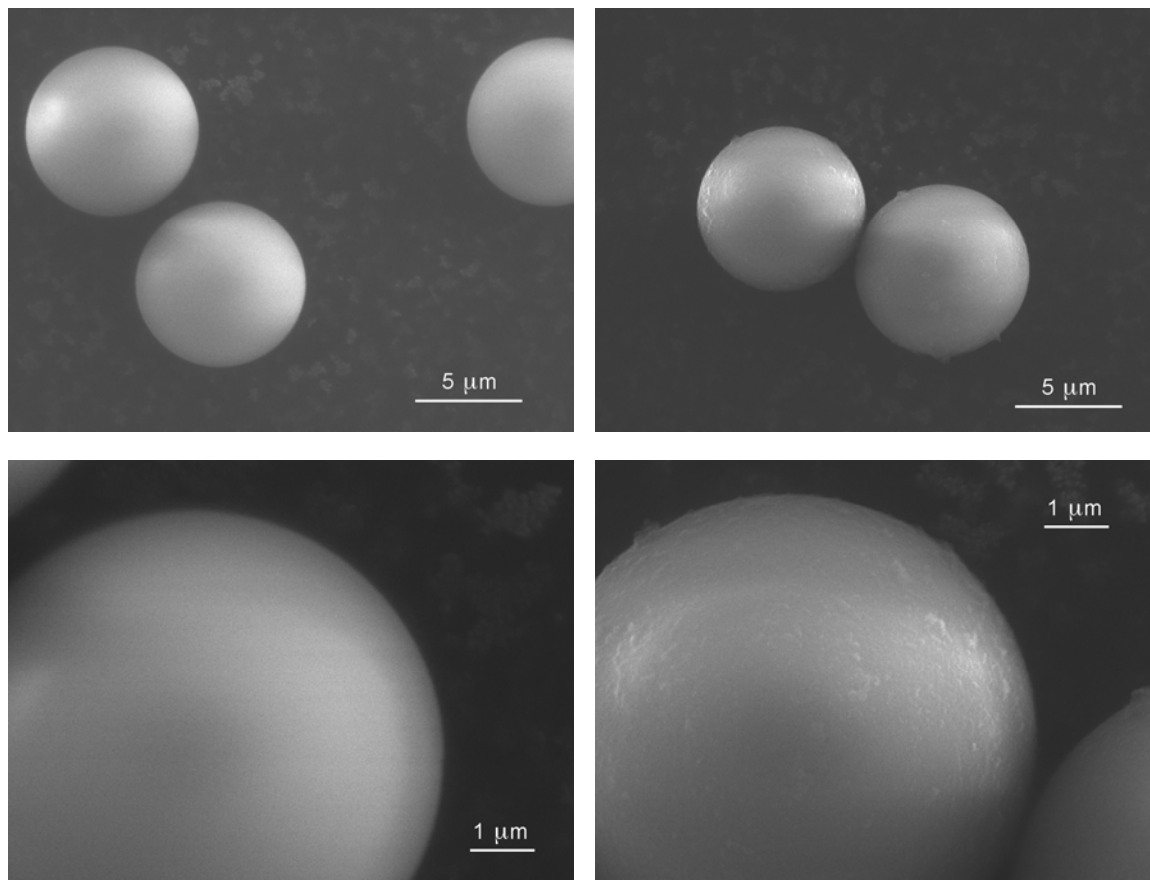


Fig. 17: SEM picture of silica microspheres. Left hand side: uncoated. Right hand side: silanised.

We produced several batches of silanised microspheres. A problem is that the coated microspheres show rather strong fluorescence, probably from residual solvent. For some batches the fluorescence signal was so strong that it overwhelmed any Raman signal from the surface coating.

We used a cw-laser at a wavelength of 532 nm to measure the spontaneous Raman scattering of the silanised silica spheres. The existence of Raman bands is required for the excitation of whispering gallery resonances. It was indeed possible to detect the Raman signal from the surface layer. Figure 19 shows the Raman spectrum of silanised silica microspheres with a diameter of 8 μm.

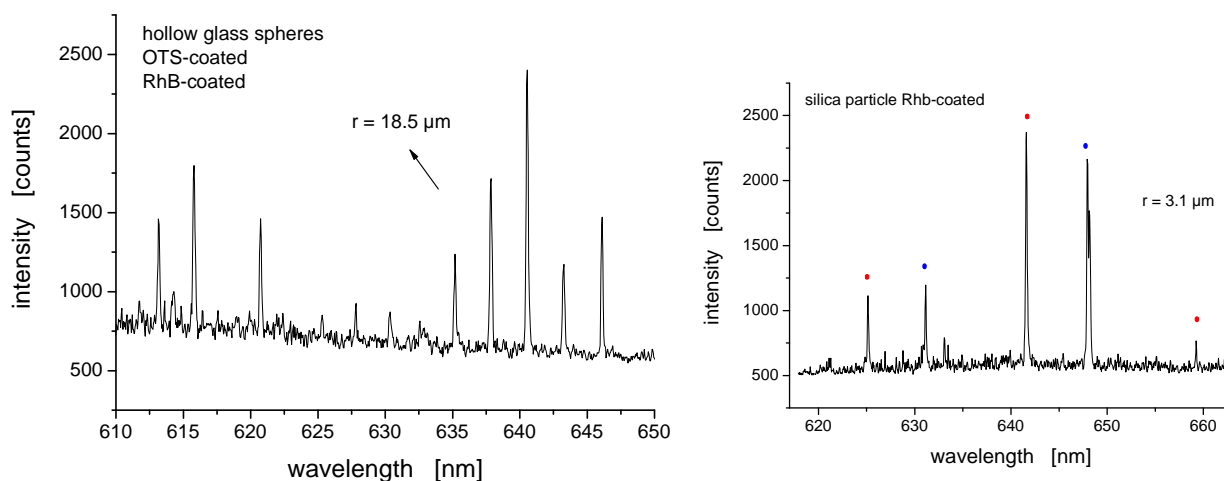


Fig. 18: cavity enhanced fluorescence spectra of a RhB-coated silanised silica sphere

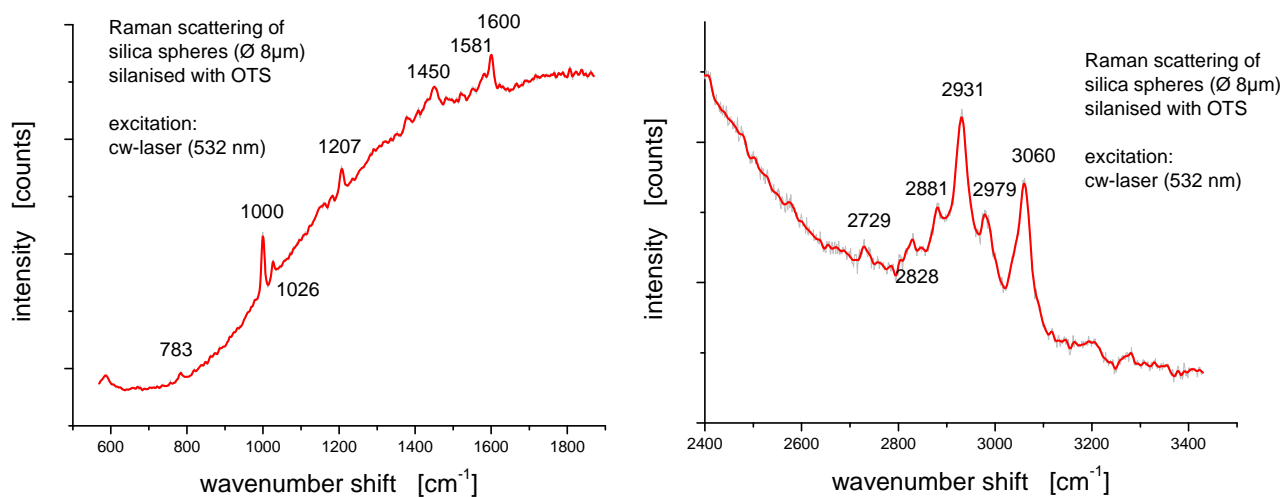


Fig. 19: Raman scattering from silica spheres silanised with OTS. 100 measurements were accumulated with an integration time of 0.5 s each.

The spectrum in fig. 19 is practically identical to the Raman spectrum of toluene (see figure 20, from [7]) which was used as a solvent for OTS during the silanising process. The toluene seems to have become attached to the microsphere surface. Although the coated particles were thoroughly pumped the toluene Raman spectrum remained.

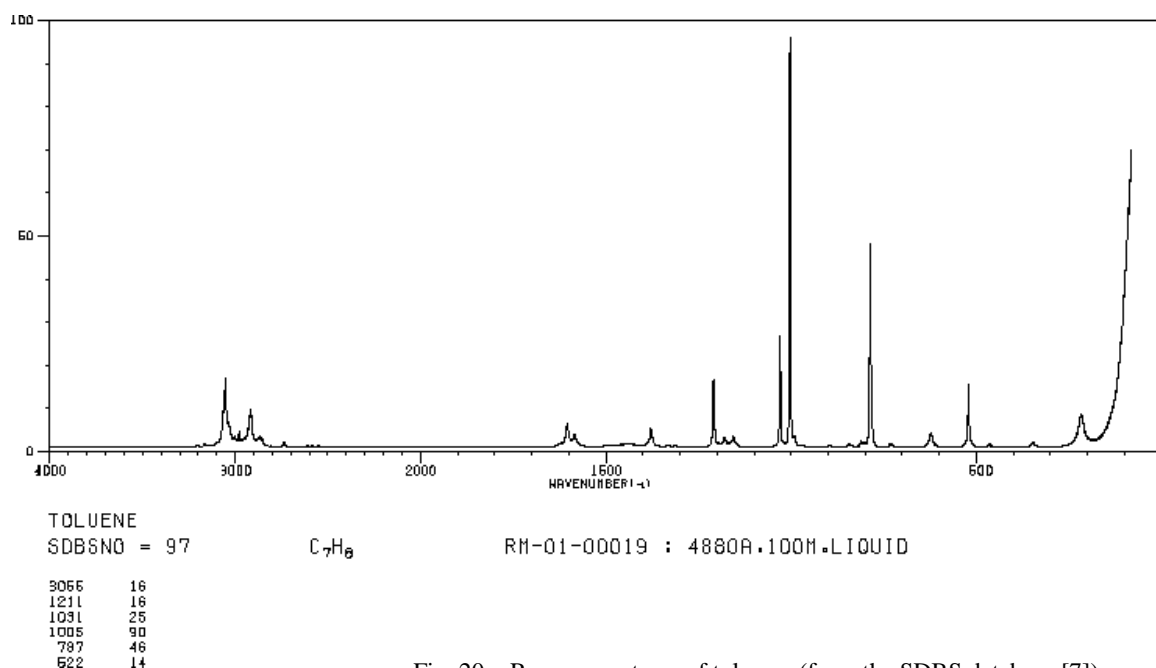


Fig. 20: Raman spectrum of toluene. (from the SDBS database [7])

Instead we found it to be more successful to silanise the microspheres without using any solvent at all. Figure 21a shows the Raman spectrum of hollow glass spheres (\varnothing ca. 30 μm) silanised with OTS without using a solvent. Peaks from the OTS show in the C-H-stretching region peaks. They agree well with spectra of OTS reported in the literature (see figure 21b, from [8]).

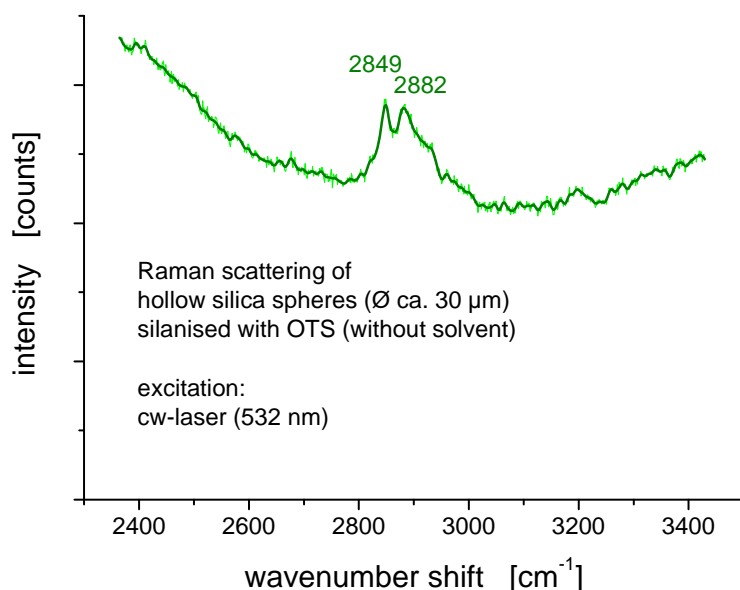


Fig. 21a: Raman scattering from hollow silica spheres silanised with OTS without using a solvent. 100 measurements were accumulated with an integration time of 0.5 s each.

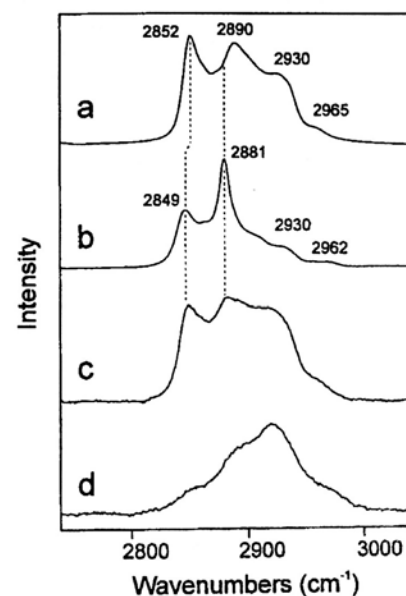


Fig. 21b: "Figure 4. Raman spectra in $\nu(\text{C-H})$ region of (a) neat liquid OTS, (b) crystalline OTS, (c) OTS attached to 3MPT-modified Ag surface, and (d) hydrolyzed 3MPT on Ag surface as a background spectrum. Integration times: (a) 15s, (b) 2 min, (c) 20 min, and (d) 20 min." [8]

At first we worked with relatively small silica spheres that had a diameter of ca. 10 μm since we could levitate those particles well in the rf-plasma. But the size plays an important role for coupling into whispering gallery mode resonances. For small particles the resonances are spaced further apart making it more difficult to couple into resonances. In the broad fluorescence spectrum of Rhodamine B coated particles which usually were used as test material it was no problem to excite resonances down to particle diameters of 6 μm . But in the much less broad Raman bands it was more difficult. It turned out that we could not excite whispering gallery mode resonances in the Raman spectrum of PMMA spheres with a diameter of 10 μm .

Therefore we had to change to larger silica spheres. We used hollow glass spheres of ca. 30 μm diameter since hollow spheres are in spite of their size still light enough that they can be levitated in the plasma.

Although the hollow glass spheres could be successfully silanised and it was possible to detect spontaneous Raman scattering from the OTS on the surface we did not succeed in measuring whispering gallery mode resonances in the Raman bands. The reason for this could be that the surface layer is not a completely closed film or is too thin.

4.3. Microspheres in an RF-plasma

The adaptive electrode (see section 3) proved to be an excellent tool for controlling the position of levitated microspheres. For the measurements microspheres were trapped above the central segment of the adaptive electrode. To achieve this, the segments of the electrode surrounding the central segment were set to a negative bias voltage of -90V, thus forming a potential well which confined the particles. These can be seen as the small group of seven bright dots in the middle of the photograph in figure 22. The particles are trapped at the position where all acting forces balance. They appear to the eye to be very stationary but if viewed with a camera with high spatial and temporal resolution it becomes clear that they move around their equilibrium position by distances at least of the order of their diameter.

The other point that complicates the alignment of the laser beam to the particles is that the photophoretic force from the laser beam pushes the particles out of the trapping region. Hence they are effectively lost after one laser shot.

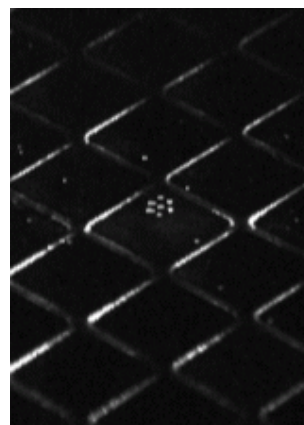


Fig. 22: MF-particles ($\varnothing 10 \mu\text{m}$) trapped above the central segment of the adaptive electrode of PULVA-INP

We were successful in obtaining cavity enhanced spectra from MF-particles that were doped with Rhodamine B. The particles had a diameter of 9.4 μm and a very smooth surface. Figure 23a shows the fluorescence spectrum obtained from such a particle levitated in an Argon rf plasma.

The signal level is not much above the noise level, but it shows a clear periodicity of ca. 10 nm. This becomes much more obvious if we look at the autocorrelation function of the signal (see fig. 23b). The periodicity which can be determined (9.3 nm) corresponds very well to the theoretically expected distance between cavity resonances of consecutive mode numbers for microparticles of this size (9.4 nm).

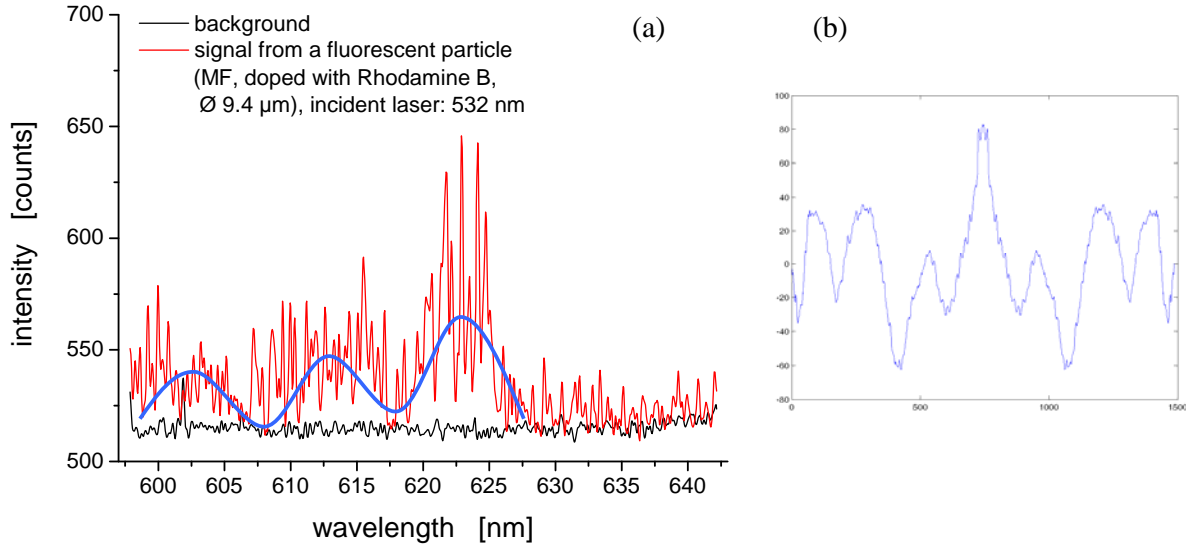


Fig. 23: a) cavity enhanced fluorescence spectrum of a Rhodamine-B-doped MF sphere levitated in an Argon plasma
b) autocorrelation function of the signal

Figure 24 shows some spectra of Rhodamine-B-doped MF spheres where individual resonances could be assigned and were used to calculate the particle radius.

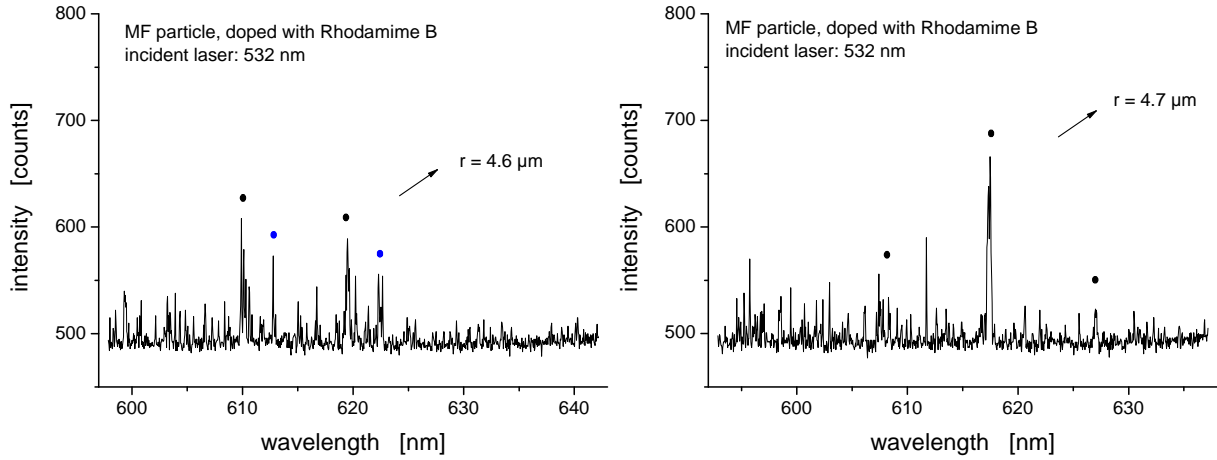


Fig. 24: Cavity enhanced fluorescence spectra of Rhodamine-B-doped MF spheres levitated in an Argon plasma.

It was extremely difficult to excite whispering gallery mode resonances on microspheres levitated in the plasma. One reason is the great difficulty of aligning the laser exactly to the particles, since the particles are not completely stationary and are lost after one laser shot due to the photophoretic force of the laser beam. The ratio of particles that are hit by the laser beam and measured whispering gallery mode spectra is very low. Therefore we used a large number of levitated particles. In the plasma environment there are other influences that might play a role. The microspheres are levitated inside a relatively strong electric field. Also they carry a large negative charge. It is possible that the particle charge or the electric field influences the interaction of the laser beam with the particles.

Conclusions / Outlook

Suitable particles in size and composition have now been identified from our investigations. Silica particles are the most suitable. Silica is a good substrate material for coating: it shows no cavity enhanced Raman scattering itself but is smooth enough to support whispering gallery mode resonances. The silica spheres were coated with hydrocarbon layers by silanising with OTS. We were able to detect the spontaneous Raman scattering from the deposited layer.

Major changes to the optical setup of the detection system have been carried out since the last report, which enable us to perform spatially resolved measurements and increased the detection sensitivity. For measurements on microspheres levitated in the plasma we have improved the signal-to-noise ratio by using a large lens to collect as much scattered light as possible.

Measurements on microspheres levitated in the rf-plasma proved to be very difficult. We made successful measurements of whispering gallery modes in the broad fluorescence band of Rhodamine-B-doped MF particles levitated in the plasma, but not so far in the narrower Raman bands of PMMA spheres or silanised silica spheres.

Further investigations are underway in order to understand the influence of the particle charge or the electric field in the plasma on the excitation of whispering gallery mode resonances. In addition we expect to study two new variants of microsphere in the next few weeks. Firstly, 30 μm hollow PMMA spheres, which should be light enough to levitate in the plasma unlike the solid PMMA spheres of the same size. Secondly, hollow silica spheres in which Rhodamine dye has been impregnated in the skin of the silica shell. This should provide much stronger WGM modes in the dye fluorescence i.e. much stronger than those shown in figure 32.

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I certify that there were no subject inventions to declare during the performance of this grant.